

Self assembling of Poly(3-hexylthiophene) (P3HT).

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Abstract

We study the assembling of P3HT chains in vacuo by means of a combination of first principles density functional theory and model potential molecular dynamics. We find that, in the absence of any external constraints, the $\pi - \pi$ interchain interaction between thiophenes is the major driving force for the assembling. Single chains stack in a staggered geometry giving rise to the formation of two-dimensional hydrophobic foils. These, in turn, assemble into a zig-zag bulk polymer structure in agreement with experimental findings. Finally, in the presence of some external constraint (like e.g. a substrate), when the alignment of single chains is favored instead of the stacking, a different bulk structure is possible where thiophene rings are aligned.

Introduction

Semiconducting polymers are promising materials for a variety of applications in organic electronics^{1,2} due to their unique combination of opto-electronic properties, ease of fabrication, and low cost manufacturing. Among them, poly-3-hexylthiophene (P3HT) is one of the most extensively studied conjugated polymer because of its relatively high carrier mobility ($0.1 \text{ cm}^2 \text{ V/s}$) coupled with solution processability³⁻⁵. P3HT applications run from light-emitting diodes⁶ to thin-film transistors.⁷ Moreover, P3HT coupled with inorganic materials (e.g. TiO_2 ,^{8,9} ZnO ,¹⁰ carbon nanotubes,¹¹ phenyl-C61-butyric acid methyl ester¹²) is an excellent component for use in low-cost photovoltaics. P3HT-based solar cells have reached power conversion efficiencies of about 5%.¹²

It was observed that when cast from solvents into thin films, P3HT self-assembles into oriented microcrystalline domains (10-50 nm) and amorphous regions.^{13,14} The larger the crystallinity, the higher is the carrier delocalization, as well as mobility. According to X-ray diffraction experiments¹³⁻¹⁹ several P3HT equilibrium crystal structures have been proposed. However, the morphological disorder occurring in polymeric systems, mainly due to the presence of multiple phases, makes the data interpretation a difficult task. Crystalline P3HT consists of a lamellar structure where the planar polymer molecules are stacked on top of each other. Two different stacking configurations have been proposed, namely: the "aligned" one²⁰ where the thiophene rings of two

stacked molecules are perfectly aligned on top of each other and the "staggered" one,¹³ where the molecules are shifted by one thiophene unit along the backbone ([figure][1][1]). Besides the chain stacking, also the relative orientation of molecules belonging to different stacks is a matter of debate and several models have been proposed. In particular, in the configuration hereafter referred to as "parallel", the hexyl chains and the thiophene rings are parallel,^{19,21} while in the so called "zigzag" the hexyl chains and the thiophene rings are guessed to form a sort of zigzag structure.¹⁵

The detailed knowledge of the polymer structure is fundamental since the actual atomic configuration strongly affects the conduction properties: for instance, it has been shown that the aligned configuration favors the interchain hole mobility,²¹ while the intrachain mobility along the backbone is strongly improved by the chain planarity.²²

In the last few years several atomistic simulations have been performed on P3HT in order to help the interpretation of the X-ray diffraction experiments.^{23–27} First principles density functional theory (DFT) calculations²³ have been applied to compare the energetics of the ideal staggered and aligned configurations at zero temperature. In particular, it was observed that the staggered configuration is slightly more stable with respect to the aligned one, mainly due to a favorite spatial distribution of the side chains. Nevertheless the calculated energy differences between the two phases at zero temperature are quite small (0.45 eV/monomer) and different phases (as well as relative stability) can be expected at finite temperature as a result of entropic contributions (e.g. the disorder of the hexyl chains). As a matter of fact, a new polymer structure (where the hexyl chains are tilted with respect to the plane of the thiophenes) was identified by model potential molecular dynamics (MPMD) at room temperature.²¹

In this work we explore an alternative theoretical approach based on a combination of DFT and MPMD, in which the P3HT bulk structure is assembled in vacuo at finite temperature from its molecular constituents. We study in this way the dominant assembling mechanisms and the resulting P3HT structures. In particular, we identify and thoroughly characterize a new structure which is similar to experimental results.¹⁵

Theoretical framework

We combine DFT and MPMD to study both the equilibrium structure of P3HT at $T=0$ K and the polymer assembling at finite temperature.

The DFT calculations have been performed by considering an orthorombic unit cell containing two stacked main chains disposed either in the aligned or staggered configuration having in total 100 atoms each (see [figure][1][1]). The geometries were fully relaxed with the aligned inversion iterative subspace method (DIIS)²⁸ by using the CPMD code²⁹ and norm conserving Martins-Troulliers pseudopotentials.³⁰ The electronic wavefunctions were expanded in a plane wave basis set with a kinetic energy cutoff of 70 Ry. The exchange correlation energies were calculated using the LDA functional.³¹ The results obtained with the CPMD code were further validated by performing the same calculations using the Quantum Espresso package³² on a limited number of selected structures. The results were very similar with both codes.

All the configurations relaxed with DFT were further optimized by means of MPMD with a minimization procedure combining both local conjugate gradients minimization and low temperature molecular dynamics as described elsewhere.³³ Simulations were performed with the DL_POLY³⁴(version 2.19) code by using the AMBER force field.³⁵ The equations of motion were integrated using the velocity Verlet integrator, with a time step of 0.5 fs. Long-range electrostatic forces were evaluated using a particle mesh Ewald algorithm.³⁶ A cutoff as large as 9.5 Å was used in order to accurately calculate the Van der Waals interactions. The atomic partial charges were calculated at DFT level from the electrostatic potential (ESP).³⁷ We then performed finite temperature molecular dynamics on a set of models of increasing dimension containing up to 14400 atoms. In order to control the temperature we used the Berendsen thermostat using a relaxation time of 0.5 ps.

Results and discussion

The assembling of two P3HT chains can be driven by two main contributions: the $\pi - \pi$ interaction which promotes the parallel stacking of different chains or the chain interdigitation which promotes the chains alignment in the same plane. In order to accurately compare the two contributions and to identify the major driving force to assembling, we investigated by first principles the polymer energy dependence on the interchain separation.

We considered an orthorhombic unit cell of P3HT with cristallographic vectors lying respectively in the alkyl side chains (a), stacking (b) and backbone (c) directions (see [figure][1][1]). Starting from an ideal planar P3HT crystal structure either in the aligned or staggered configurations, we performed a series of 240 geometry optimizations on unit cells of different volumes by varying the lattice parameters a and b in the range 14.2-16.2 Å (15.0-16.2 Å for the staggered) and 6.8-10.0 Å both for the aligned and staggered configurations. The value of c was obtained by optimizing an isolated chain and then kept fixed at 7.75 Å. [figure][2][2] shows the corresponding energy landscapes as a function of a and b for the aligned (left) and staggered (right) configurations. In both the staggered and aligned configurations the energy profile along the b direction (which is the direction where the $\pi - \pi$ interactions occur) shows a larger variation (~ 0.5 eV/monomer) and a well defined minimum; on the other hand, the energy variation along a is less pronounced (as small as ~ 0.1 eV/monomer), indicating a weak interaction between neighboring chains due to the interdigitation of the hexyl groups. This allows us to conclude that the $\pi - \pi$ interactions actually drive the P3HT assembling.

The aligned configuration shows two minima. The global one occurs at $a=14.5$ Å and $b=7.8$ Å corresponding to a high degree of interdigitation (the interchain distance along the hexyl chains is 14.5 Å). The thiophene rings turn out to be inter-twisted along the backbone. Such a configuration, though theoretically possible at $T=0$ K, corresponds to a very high dense P3HT, never observed in real systems. The second minimum, hereafter named as aligned structure (A), falls closer to the experimental data at $a=15.4$ Å and $b=7.6$ Å. In this case the thiophene rings along each polymer chain lie parallel (see [figure][1][1], left panels).

The staggered configurations ([figure][2][1], right) show only one minimum at $a=15.2 \text{ \AA}$ and $b=7.6 \text{ \AA}$, the corresponding structure having the thiophene rings almost on the same plane (see [figure][1][1], right panels).

The equilibrium lattice parameters for both the aligned and staggered configurations are in good agreement with the experimental values: $16 \text{ \AA} \leq a \leq 16.8 \text{ \AA}$, $7.66 \text{ \AA} \leq b \leq 7.8 \text{ \AA}$, $7.7 \text{ \AA} \leq c \leq 7.8 \text{ \AA}$.^{13–18,23} The largest deviations are found for the a value as a result of the high interdigitation that is possible only at $T=0 \text{ K}$ due to the missing thermal vibrations. We will show below that at room temperature the vibrational motion of the hexyl chains hinders the interdigitation bringing to an average interchain distance of 16.2 \AA in agreement with the experimental values. A comparison between the aligned and staggered energy minima shows that the two configurations are almost isoenergetic (in agreement with previous calculations), with an energy difference of 0.125 eV/monomer .

The above first-principles analysis is conceptually important in order to identify the interchain interactions. However, because of computational limits, all the calculations were performed at $T=0 \text{ K}$, so neglecting the role of thermal disorder in the polymer phase. In order to include thermodynamics we made use of less computationally demanding MPMD to perform suitably long ($\sim 1 \text{ ns}$) finite temperature simulations on larger systems (up to 10^4 atoms). The accuracy of the MP requires a fine tuning of the atomic partial charges that we achieved by the following first-principles procedure. We calculated the atomic partial charges at DFT level (see the methodology section) by embedding a single P3HT monomer (two thiophenes with the relative hexyl chains, 50 atoms in total) in a bulk-like system formed by three P3HT stacked chains (300 atoms) in the aligned structure. We further imposed the symmetry by averaging the charges on the corresponding atoms. By using the calculated atomic charges, the dipole moments have been calculated for isolated molecules, corresponding to the unit cells at equilibrium reported in [figure][1][1]. The results show that the dipole moment for the CPMD-generated A structure is oriented along the molecule backbone (see [figure][1][1]) with a module of 2.065 Debye , while the dipole moment for the staggered structure is very small (just 0.195 Debye) and oriented along the hexyl chains. We stress that the partial

charges calculated without the embedding are quite different giving results unsuitable for the bulk.

We validated the above model potential (Amber force field with partial charges calculated as above) by recalculating the energy basins as a function of the lattice parameters. An overall agreement was found with the DFT results. Similarly to the DFT case, the MPMD data show two minima for the aligned configuration and one minimum for the staggered configuration. The equilibrium lattice parameters are $a=15.8 \text{ \AA}$, $b=8.0 \text{ \AA}$ and $c=7.75 \text{ \AA}$ for the aligned configuration and $a=15.5 \text{ \AA}$, $b=8.0 \text{ \AA}$ and $c=7.75 \text{ \AA}$ for the staggered configuration in good agreement with experiments. Once again, the aligned and staggered configurations are almost isoenergetic with an energy difference of 0.063 eV/monomer.

P3HT assembling

In this Section we aim at identifying finite temperature realistic models of bulk polymers other than the ideally interdigitated structures characterized above. Nevertheless, we find that the aligned structure is stable and perfectly interdigitated even after 1 ns-long annealing at $T=300\text{K}$.

Here, in order to find other stable phases, we follow an alternative path and we focus on the assembling of P3HT chains in vacuo. The building block of our analysis is a single P3HT chain, extending indefinitely along the backbone direction. Firstly we study the stacking of the polymer chains. To this aim, two chains are put at different distances and relative orientations and their interaction is studied by performing 100 ps-long MD runs at $T=300 \text{ K}$. In the final state, the two chains always stacked on top of each other thus confirming that the $\pi - \pi$ interaction is the driving force for the P3HT assembling. Moreover, the staggered configuration was found to be largely favored (and in fact found at the end of any simulation). By further stacking P3HT chains, two-dimensional structures (hereafter named h-foils) are eventually formed (see [figure][3][3]). The h-foils have hydrophobic surfaces (h-surfaces) formed by the hexyl chains. Moreover, the h-foils give rise to a perfectly staggered stacking. This is an important result since the direct alignment at $T=0 \text{ K}$ is the lowest energy configuration for a perfectly interdigitated bulk, while, for two-dimensional structures at room temperature, the staggered configuration is favored. The above

result is confirmed by the fact that, at $T=300$ K, an h-foil initially put into an A aligned configuration, always spontaneously switches to the staggered one. Finally, by assembling an increasing number of two-dimensional h-foils it is possible to generate a bulk polymer (see [figure][3][3]).

The interaction of the h-foils was studied at finite temperature (see [figure][4][4, top]). First of all we put two separated foils at 50 \AA distance and we observed their spontaneous organization into bilayers. The thiophene rings in the two layers tilt as a result of a long range interaction with the other foil. In particular, it was found that the thiophene rings belonging to adjacent h-foils formed in a zigzag-like configuration (see [figure][4][4, top]). Moreover, this configurations showed a low degree of interchain interdigitation, the equilibrium distance between h-foils was 16.2 \AA in agreement with the experimental results. By replicating the final configuration of [figure][4][4] a model of P3HT bulk structure was obtained. We found that the corresponding bulk structure was stable at $T=300$ K (see [figure][5][5]). Moreover, the corresponding total energy, obtained by minimizing the final structure, is lower than the corresponding total energies for the aligned and shifted configurations by 0.2 eV/monomer . This crystalline phase corresponds to the one previously proposed by Prosa et al.¹⁵

This assembling mechanism (hereafter named as "h-mechanism"), ignited by the stacking of two P3HT chains, will occur in absence of any constraint. Moreover, if we suppose the presence of some constraint (like e.g. a substrate) promoting the alignment of two P3HT chains (instead of the stacking), the scenario completely changes. In this case we refer to an s-foil the system formed by the alignment of an infinite number of P3HT chains (see [figure][3][3]). In order to investigate the assembling of several s-foils, we simulated the stacking of a single s-foil on top of an aligned substrate (see [figure][4][4, bottom]). In this case we found that the s-foil preserves the aligned stacking giving rise to an aligned P3HT crystal. We refer to this assembling mechanism as the s-mechanism (see [figure][3][3]).

P3HT surfaces

According to the above analysis, the h-surfaces are likely to occur in P3HT. In this Section we calculate their formation energy and their long-range electrostatic interaction. To this aim, we cut several slabs (formed by an increasing number of layers) out from a polymer bulk, along the h-surfaces. We considered both staggered or aligned P3HT. Periodic boundary conditions are applied to each slab by fixing to 15 nm the distance between the surface replicas. After 0.5 ns-long MD annealing at low temperature, each system was relaxed by conjugate gradients. This procedure is necessary to properly relax the hexyl chains. The calculated energies $E(N)/N$ (normalized to the number of layers N) are reported in [figure][6][6] as a function of N . The energy $E(N)$ of a slab is the sum of three terms:

$$E(N) = 2\gamma + E_B N - A_0 N^2 \quad (1)$$

the energy 2γ of its two surfaces, its cohesive bulk energy $E_B N$ (E_B is the bulk energy per layer), and the electrostatic energy due to the interaction with replicas that scales as N^2 with the number of atoms of the slab. γ , E_B and A_0 are used as adjustable parameters to reproduce the atomistic data. The best fit of atomistic data are reported as lines in [figure][6][6]. E_B was found to be lower in the aligned case (-6.2 eV) than in the staggered one (-5.59 eV), consistently with the DFT and MPMD results for the bulk. γ was found to be 2.52 eV (3.06 eV) for the aligned (staggered) h-surface. According to this analysis, the assembling of two h-terminated semibulk is more exothermic in the staggered case. This is consistent with the observed reactivity between staggered h-foils. The A_0 values are 0.026 eV and 0.033 eV for the aligned and staggered h-surfaces, respectively. This means that the staggered h-surfaces have larger interactions than the corresponding aligned one.

Conclusions

In conclusion, we have identified the $\pi - \pi$ as the main contribution for the P3HT self assembling by means of first principles DFT calculations. We further studied the P3HT assembling at finite temperature by means of MPMD and we identified two different assembling mechanism giving

rise to different final P3HT structures. In absence of constraints, the P3HT single chains will stack on h-foils, which at finite temperature are found in the staggered configuration. The successive assembling of h-foils is predicted to give rise to a bulk structure in a zigzag configuration, as in fact experimentally supported. Furthermore we studied an alternative assembling mechanism which will occur in the presence of some constraint (i. e. a substrate) which favors the alignment of P3HT chain instead of their stacking. In this case we predict the occurrence of an aligned crystal structure.

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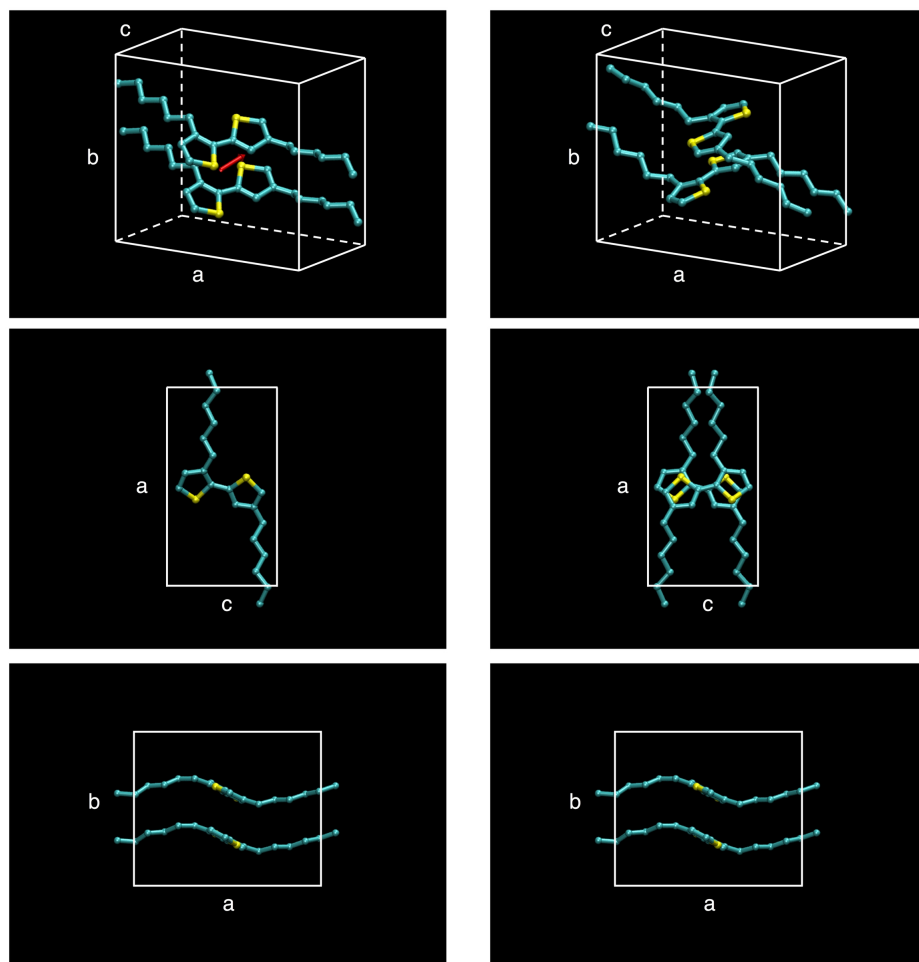


Figure 1: Perspective-view (top), top-view (middle) and side-view (bottom) of P3HT equilibrium structures obtained by DFT for the aligned (left) and staggered (right) configurations. The white box represent the orthorhombic unit cell with the corresponding lattice parameters. The red arrow in the top panel indicates the dipole moment.

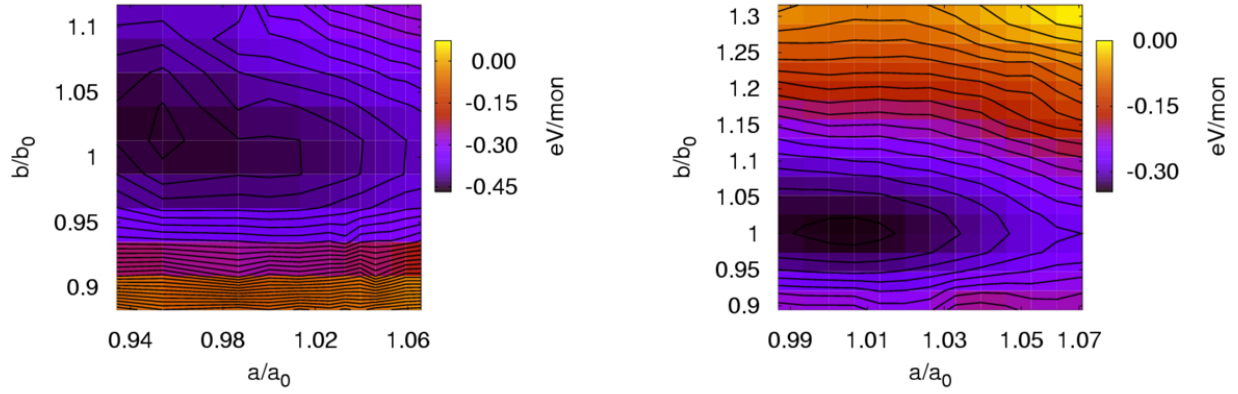


Figure 2: Energy landscapes obtained by DFT for the aligned (left) and staggered (right) phase respectively. The lattice parameters are referred to the equilibrium values a_0 and b_0 while the total energy is referred to the energy of two unbound chains.

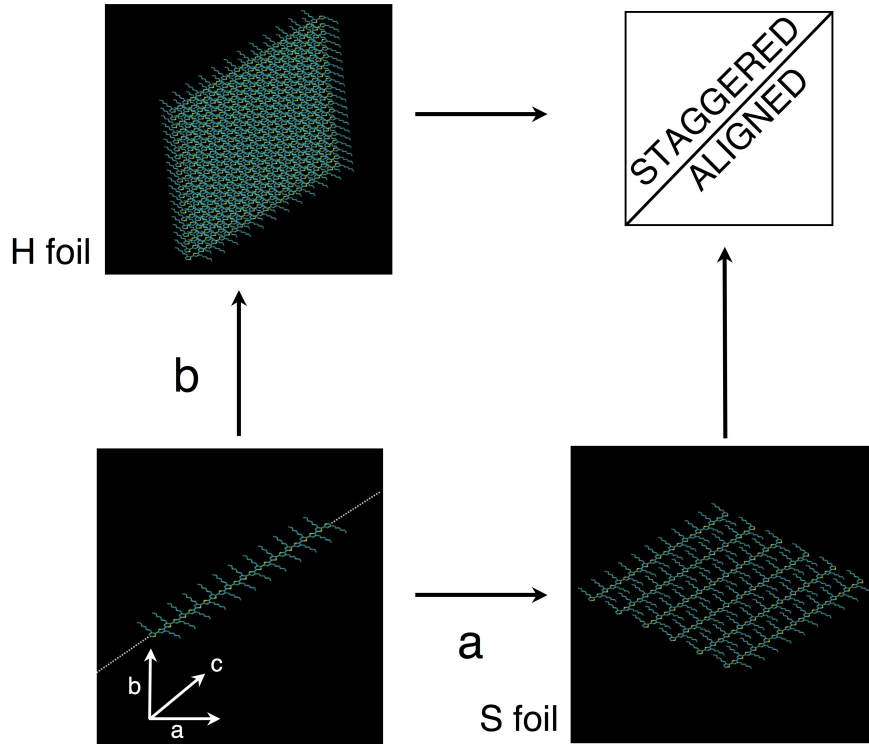


Figure 3: Flow chart of the two assembling mechanisms proposed. In the h-mechanism the assembling of single P3HT chains (lower left) is driven by the $\pi - \pi$ interactions, resulting in the formation of h-foils (upper, left). The successive h-foils assembling gives rise to staggered structures. In the s-mechanism the assembling brings to the formation of s-foils (lower right) and their successive stacking gives rise to aligned structures.

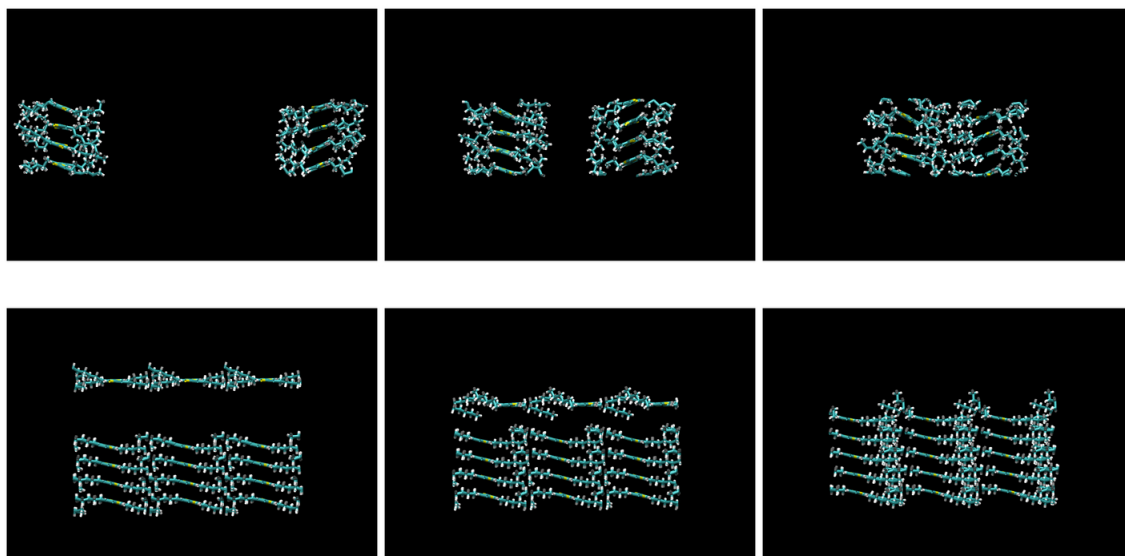


Figure 4: Successive MD snapshots corresponding to the assembling mechanisms proposed. In the h-mechanism (top), two h-foils assemble in a zigzag-like final structure. In the s-mechanism (bottom) one s-foil stacks on top of a P3HT semi bulk in the aligned final structure.

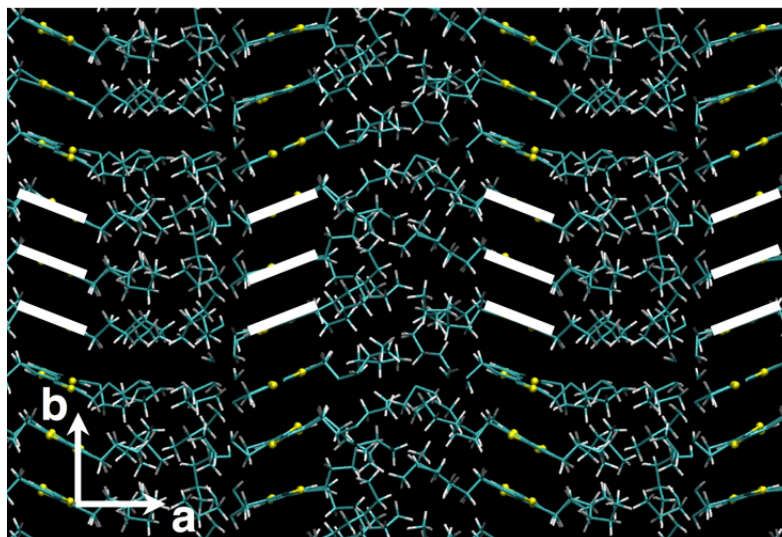


Figure 5: Side view of the final zigzag configuration obtained after 1 ns of MD simulation at $T=300$ K. A zigzag-like structure between the thiophene rings corresponding to different layers is observed.

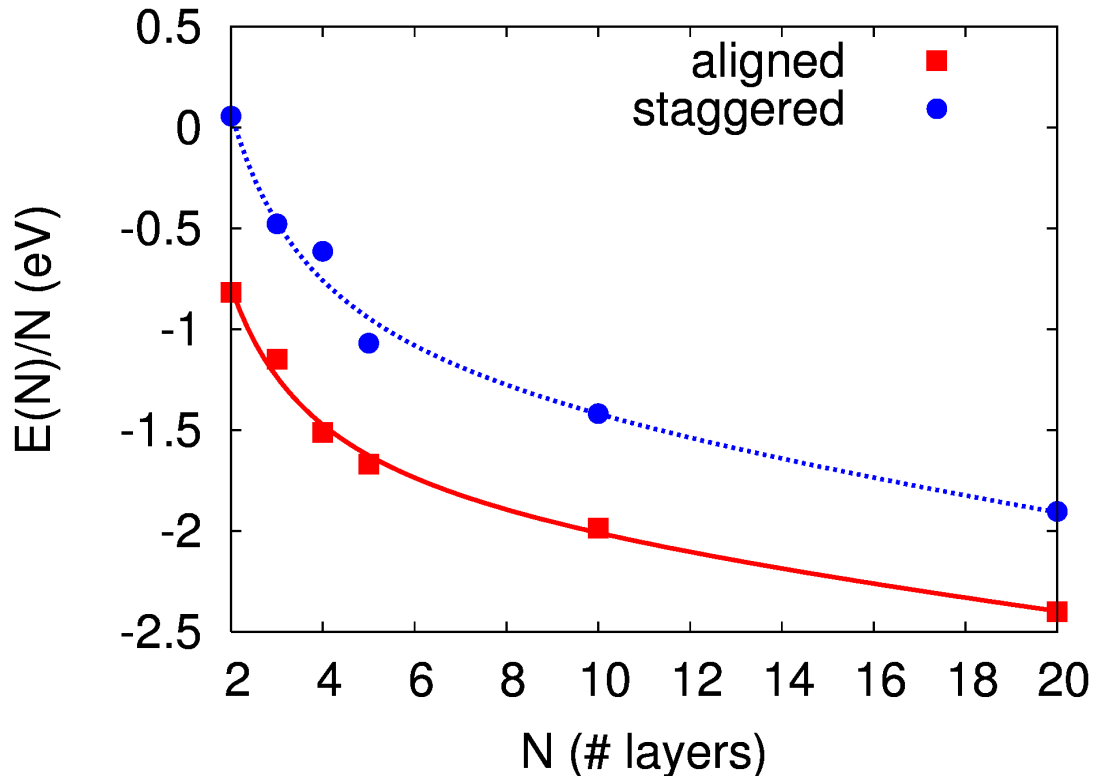


Figure 6: Total energy (normalized to the number of layers N) $E(N)/N$ of a P3HT slab formed by a number of layers in the range 2-20. We considered both the cases of initially staggered or aligned configurations. The atomistic data are represented as red squares and blue dots. Lines correspond to the calculations based on the continuum model.